

# **De filterfunctie van het Eemsestuarium voor opgelost anorganisch stikstof (DIN), opge- lost anorganisch fosfaat (DIP) en silicaat**

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## Samenvatting

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### KADER

Dit rapport is één van de geplande producten van het project HERSTEL. De doelstelling van het project was om, ter voorbereiding van de volgende nota waterhuishouding, een evaluatie te maken van de ecologische gevolgen van de reducties in nutriëntenvrachten.

Om deze evaluatie goed te kunnen uitvoeren is het ondermeer noodzakelijk om te kunnen vaststellen hoeveel nutriënten er in het menggebied tussen rivier en zee achterblijven. In dit rapport wordt ingegaan op de filterfunctie van het Eems estuarium.

### Beleidsrelevantie

Reductie van nutriëntenvrachten via rivieren behoeft niet onmiddellijk te leiden tot reductie van de nutriëntenfluxen naar het kustwater van de Noordzee, omdat een deel van deze verbindingen óf in de bodemsedimenten kan worden opgeslagen (stikstof ingebouwd in organisch materiaal en/ of als geadsorbeerd ammonium aan bodemdeeltjes; fosfor in de vorm van allerlei organische en anorganische verbindingen en/of geadsorbeerd aan bodemdeeltjes) óf aan het systeem kan ontsnappen (stikstof via denitrificatie). In beide gevallen zou men van een filterfunctie kunnen spreken.

Goede vrachtberekeningen zijn alleen mogelijk als we weten welk deel van de riviernutriënten in het mondingsgebied achterblijft.

Het onderhavige rapport geeft voor de wintersituatie kwantitatieve antwoorden op bovenstaande vragen.

Naast de nutriënten wordt ook het gedrag van opgeloste organische verbindingen en enkele aan nutriënten gerelateerde elementen (Al, Fe) behandeld.

### INLEIDING

Als een in rivierwater opgeloste stof via een estuarium in zeewaartse richting wordt getransporteerd dan kunnen er in principe drie dingen met deze opgeloste stof gebeuren.

1. De stof reageert niet met zeewater en de in het estuarium aanwezige zwevende stof. In dit geval kan de verdeling in het estuarium worden beschreven als een functie van het zoutgehalte. Uitgezet tegen het zoutgehalte laat de concentratie van de stof een lineaire afhankelijkheid van het zoutgehalte zien. Men spreekt dan van conservatief gedrag. Variaties in de tijd van de rivierconcentraties kunnen, in relatie tot de tijdschalen van de watermenging, leiden tot een convex mengdiagram (toenemende concentraties) of tot een concaaf mengdiagram (afnemende concentraties).

Reageert de betreffende stof echter met zwevende stof of treden er onder invloed van de ionsamenstelling in het zeewater bepaalde fysisch-chemi-

sche reacties op dan spreekt men van niet-conservatief gedrag en zijn er twee mogelijkheden:

2. Wordt de betreffende stof verwijderd (bijvoorbeeld via adsorptie aan zwevend organisch en anorganisch materiaal) dan heeft het mengdiagram een concave vorm.
3. Raakt de betreffende verbinding weer gemobiliseerd van de zwevende stof (het raakt gedeeltelijk weer in oplossing via desorptie processen) dan zal het mengdiagram een convexe vorm hebben.

Het is belangrijk erop te wijzen dat bij langere verblijftijden van het rivierwater in het estuarium, een continu toenemende concentratie van een bepaalde verbinding in het aangevoerde zoete water vanwege het daardoor veroorzaakte concave mengdiagram leidt tot een schijnbaar niet-conservatief gedrag.

In dit rapport wordt de filterfunctie van het Eems estuarium voor nutriënten besproken. We baseren onze analyse op vaartochten, die in het kader van EFFEMIS Herstel van februari 1992 tot juni 1993 werden uitgevoerd. We beperken ons tot de wintersituatie 1992/1993

Deze keus is om de volgende redenen gemaakt:

- 1 In de winter spelen biologische processen geen belangrijke rol;
- 2 De serie van vier winter tochten maakt het mogelijk om minstens ten dele het effect van variaties in de input van nutriënten via Eems en Westerwoldsche Aa op de nutriëntengradient in het estuarium op te vangen.

## **MATERIAAL EN METHODEN**

Aantal en ligging van de monsterstations (Figuur 1) en de monsternamen zijn beschreven door VAN BEUSEKOM & DE JONGE (1994) in het hierachter gehechte manuscript beschreven. De vier wintertochten vonden op 24-25/11/1992, 9-10/12/1992, 12-13/01/1993 en 9-10/2/1993 plaats. De nutriënten analyses werden door het Rijkswaterstaat, RIKZ/Laboratorium te Middelburg uitgevoerd. De monsternamen werden uitgevoerd door de Meetdienst Oost (Delfzijl) van Directie Noord-Nederland met het vaartuig "Van Veen".

Om de filterfunctie van het estuarium voor de hier onderzochte verbindingen vast te stellen is gebruik gemaakt van lineaire regressieanalyse tussen concentratie en zoutgehalte. Voor ieder van de tochten werd het snijpunt van de regressielijn met de Y-as (nutriënten concentratie bij een zoutgehalte van 0 PSU) (Practical Salinity Units) berekend.

Om deze analyse uit te kunnen voeren zijn de meetresultaten uit het zoutwatergedeelte van het estuarium gebruikt.

Voor silicaat en DIN (opgelost anorganisch stikstof) zijn alle waarden van monsterstations gebruikt met een zoutgehalte hoger dan 10 PSU, omdat vanaf dat zoutgehalte altijd een nagenoeg conservatief gedrag werd gevonden. Voor DIP (opgelost anorganisch fosfaat) hebben we de punten gebruikt met een zoutgehalte hoger dan 25 PSU, omdat bij lagere zoutgehalten nog een duidelijke DIP-input (waarschijnlijk door desorptie van zwevende stof) optrad. De door extrapolatie geschatte concentratie van het betreffende element bij zoutgehalte 0 werd vergeleken met de werkelijk waargenomen rivierconcentratie.

Twee zoetwaterbronnen zijn van belang in het Eems estuarium, de rivier de Eems zelf en de Westerwoldsche Aa. De Eems voert ongeveer 10 maal meer water aan dan de Westerwoldsche Aa. We hebben op grond van dat gegeven een gewogen gemiddelde berekend van de in het estuarium uitmondende rivieren. Op grond van dit gewogen gemiddelde en de door extrapolatie verkregen waarden bij 0 PSU hebben we berekend welk percentage van de aangevoerde zoetwaternutriënten in het estuarium verwijderd dan wel extra toegevoegd worden.

## RESULTATEN EN DISCUSSIE

In de figuren 8A - 8C zijn de concentraties DIP, DIN (de som van ammonium, nitriet en nitraat) en opgelost silicaat geplot als functie van het zoutgehalte. De monsters uit de Dollard/Westerwoldsche Aa (gevulde driehoekjes) onderscheiden zich van die uit de Eems (gevulde cirkeltjes).

De verdeling van DIP (opgelost anorganisch fosfaat) toont een niet-conservatief gedrag van deze stof. Kenmerkend voor dit verschijnsel is het maximum, dat halverwege het estuarium optreedt. Bij zoutgehalten hoger dan 25 PSU treedt conservatieve menging met zeewater op.

De verdeling van DIN (opgelost anorganisch stikstof) toont alleen tijdens de tocht in december een volstrekt conservatief gedrag. Tijdens november 1992 duidt de concave vorm van de DIN-zout curve erop, dat de import van stikstof via de Eems kort voor de bemonstering is toegenomen. De convexe curves tijdens januari en februari 1993 wijzen op een afnemende aanvoer door de Eems ten opzichte van de periode daarvoor.

De grafieken voor opgelost silicaat in het gebied tussen Eemshaven en Borkum laten voor de tochten 10, 11 en 13 een lineaire samenhang met het zoutgehalte zien. De siliciumconcentraties in het zoete water blijken ongeveer 200  $\mu\text{M}$  te zijn. Tijdens de bemonstering in januari 1992 (tocht 12) wordt een afwijkend gedrag gevonden. De zeer lage concentraties in het binnengebied doen vermoeden, dat er tijdens de voorbehandeling

(ontdooien) iets is fout gegaan. De resultaten van deze tocht zijn verder buiten beschouwing gelaten.

**Tabel 1**

Vergelijking van gemiddelde concentraties nutriënten in de rivieren de Eems en de Westerwoldsche Aa met de schattingen die zijn gebaseerd op lineaire regressie analyse tussen saliniteit en nutriënten concentraties. Voor DIN en silicaat zijn de data gebruikt voor zoutgehaltes hoger dan 10 PSU. Voor DIP zijn de data gebruikt voor zoutgehaltes hoger dan 25 PSU.

	Gewogen gemiddelde concentratie in Eems en WWA	Extrapolatie naar 0 PSU $\pm$ 95% betr. interval	Regressie coëfficiënt (r) en significantie niveau (P)	Input/Retentie
	( $\mu$ M)	( $\mu$ M)		(%)
DIN	667	570 $\pm$ 24	$r^2 = 0.96$ ; $P < 0.0001$	- 15
cruise 10-13				
Silicaat	199	208 $\pm$ 6.7	$r^2 = 0.98$ ; $P < 0.0001$	+ 7
cruise 10, 11, 13				
DIP				
cruise 10	2.48	6.8 $\pm$ 1.4	$r^2 = 0.95$ ; $P < 0.0001$	+274
cruise 11	1.98	4.7 $\pm$ 0.7	$r^2 = 0.96$ ; $P < 0.0001$	+237
cruise 12	2.65	5.1 $\pm$ 1.0	$r^2 = 0.99$ ; $P < 0.005$	+192
cruise 13	1.12	4.0 $\pm$ 0.5	$r^2 = 0.99$ ; $P < 0.0001$	+357
all cruises	2.06	5.2		+252

In tabel 1 staan de resultaten van de berekeningen voor het vaststellen van de filterfunctie van het Eems estuarium samengevat.

De resultaten laten zien, dat in de winterperiode het Eems estuarium het aangevoerde DIN grotendeels doorgeeft aan de Noordzee. Ongeveer 15% wordt in het estuarium verwijderd, waarbij denitrificatie het meest voor de hand liggende proces is.

Het door de rivieren naar het estuarium aangevoerde silicaat wordt in de winter geheel aan de Noordzee doorgegeven. Bovendien wordt in vergelijking met de berekende riviervracht in het estuarium nog ongeveer 7% silicaat aan de riviervracht toegevoegd. De bron voor dit silicaat is zeer waarschijnlijk fysische oplossing/ remineralisatie van opaal (diatomeeënscalletten) dat in de groeiperiode werd ingebouwd.

DIP laat een geheel ander beeld zien. De fosfaat verdeling vertoont te allen tijde een duidelijk maximum halverwege het estuarium. Dit wijst primair op de desorptie van fosfaat van zwevende stof. De reden voor de input van opgelost fosfaat in het estuarium moet, gezien het seizoen, vooral worden gezocht in het geochemisch gedrag van fosfaat, waarvan de concentraties door evenwichten met vooral partikulair ijzeroxyhydroxide bepaald worden (FROELICH, 1986, DE JONGE & ENGELKES, 1993). Het is niet uitgesloten dat dit verloop ook nog wordt beïnvloed door fosforaccumulatie na aanvoer van partikulair materiaal vanuit vooral de zee. De via extrapolatie berekende rivierconcentraties (gewogen gemiddelde) zijn 1.9 tot 3.6 maal hoger dan de werkelijk gemeten rivierconcentraties (Tabel 1) en laten zien dat de hoeveelheid fosfaat die in de winter het estuarium verlaat aanzienlijk groter is dan de hoeveelheid die door de rivier de Eems wordt aangevoerd.

Naast het aspect van de filterfunctie is ook gezocht naar mogelijke verklaringen voor het meer gedetailleerde gedrag van de elementen fosfor, aluminium en ijzer in het Eems estuarium.

Vastgesteld is dat er in de wintermaanden stroomopwaarts van het troebelingsgebied sprake is van een persistent lokaal maximum in de concentraties fluorescentie, opgelost ijzer, opgelost aluminium en DIP. Dit is het gebied dat is gelegen in de zoetwaterzone van de rivier de Eems.

Stroomopwaarts van dit lokale maximum werden de volgende concentraties aangetroffen: fluorescentie 6 tot 9 rel. units; ijzer 0.9 tot 2.4  $\mu\text{mol dm}^{-3}$ ; aluminium 0.5 tot 0.7  $\mu\text{mol dm}^{-3}$  en DIP 0.6 tot 2.3  $\mu\text{mol dm}^{-3}$ . De maximale concentraties die werden aangetroffen waren: fluorescentie 24 rel. units; ijzer 5.8  $\mu\text{mol dm}^{-3}$ ; aluminium 1.4  $\mu\text{mol dm}^{-3}$  en DIP 8.3  $\mu\text{mol dm}^{-3}$ .

In stroomafwaartse richting vertoonde in tegenstelling tot ijzer, aluminium en DIP, de fluorescentie (een maat voor de hoeveelheid opgeloste organische stof) een conservatieve menging met zeewater.

Opgelost aluminium en ijzer verdwenen als functie van het zoutgehalte al snel uit het water (waarden tot ongeveer 100 nmol  $\text{dm}^{-3}$  aluminium en  $\sim 0.3 \mu\text{mol} \cdot \text{dm}^{-3}$  Fe bij zoutgehaltes van ca. 7 PSU).

De ijzer concentraties zakten in zeewaartse richting verder tot waarden beneden ongeveer 0.04  $\mu\text{mol dm}^{-3}$ . De concentraties opgelost aluminium daalden aanvankelijk tot ongeveer 20 nmol  $\text{dm}^{-3}$  bij 29 PSU om daarna weer toe te nemen tot waarden van ongeveer 30-44 nmol  $\text{dm}^{-3}$  bij hogere zoutgehaltes.

De DIP concentraties zakten aanvankelijk tot de waarden die ook in stroomopwaarts gelegen stations werden gevonden, maar in verder zee-waartse richting werd dit weer gevolgd door een secundair maximum in het middengebied van het estuarium (tussen mond Dollard en Eemshaven). Bij saliniteiten hoger dan 25 PSU vertoonde het DIP conservatieve menging met zeewater (zie boven).

Op grond van de verkregen resultaten denken we dat veranderingen in adsorptie-desorptie evenwichten verantwoordelijk zijn voor de gevonden maxima in fluorescentie, ijzer, aluminium en DIP. De overeenkomsten tussen de verschillende curven suggereert dat hetzelfde type mechanisme daarvoor verantwoordelijk is. Mogelijk is dit proces gerelateerd aan het ontstaan van nieuwe evenwichtsinstellingen wanneer bijvoorbeeld marien slib (via natuurlijke processen) terecht komt in de zoetwaterzone (met een ionsamenstelling die zeer sterk verschilt van die van zeewater) van het estuarium en/ of als zoetwaterslib terecht komt in de brakwaterzone van het estuarium.

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# 1 Abstract

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In winter 1992/1993, a persistent local maximum in fluorescence, dissolved iron, dissolved aluminium and dissolved inorganic phosphate was found, upstream of the turbidity maximum in the freshwater zone of the Ems estuary (The Netherlands - Federal Republic Germany; western Europe). Upstream of this local maximum values ranged from 6 to 9 rel. units fluorescence, 0.9 to 2.4  $\mu\text{mol dm}^{-3}$  iron, 0.5 to 0.7  $\mu\text{mol dm}^{-3}$  aluminium and 0.6 to 2.3  $\mu\text{mol dm}^{-3}$  dissolved inorganic phosphate. Within the maximum peak values of 24 rel. units fluorescence, 5.8  $\mu\text{mol dm}^{-3}$  iron, 1.4  $\mu\text{mol dm}^{-3}$  aluminium and 8.3  $\mu\text{mol dm}^{-3}$  dissolved inorganic phosphate were observed.

Downstream, fluorescence (indicator of dissolved organic carbon) showed conservative mixing with sea water, whereas, dissolved iron, aluminium and dissolved inorganic phosphate did not. Dissolved aluminium and iron were quickly removed from solution to reach values of  $\sim 100 \text{ nmol dm}^{-3}$  aluminium and  $\sim 0.3 \mu\text{mol dm}^{-3}$  Fe at salinities of approximately 7 PSU. Further seaward, iron concentrations gradually decreased to levels below  $0.04 \mu\text{mol dm}^{-3}$ . Dissolved aluminium first decreased to  $\sim 20 \text{ nmol dm}^{-3}$  at 29 PSU and increased again to concentrations of 30-44  $\text{nmol dm}^{-3}$  at higher salinities. Dissolved inorganic phosphate, however, first decreased to upstream concentrations before reaching a secondary peak in the mid-estuarine reaches. At salinities  $>25$  PSU dissolved inorganic phosphate mixed conservatively with sea water.

It is hypothesized that adsorption-desorption equilibria are responsible for the local maximum values of fluorescence (DOC), iron, aluminium and dissolved inorganic phosphate. The similarity between the observed curves suggests a common underlying process, possibly related to the adjustment of new equilibria between suspended matter of marine and riverine origin.



## 2 Introduction

Since the 1960s, nitrate and dissolved inorganic phosphate concentrations in inland waters have increased as a result of the use of artificial fertilizers in agriculture and increasing concentrations in domestic and industrial wastewater. In contrast, dissolved silicate concentrations remained practically unchanged (e.g. VAN BENNEKOM and WETSTEIJN, 1990). This was considered to have caused an increase of phytoplankton biomass, primary production and to a shift in the species composition of phytoplankton in the estuaries and coastal areas of the North Sea (WEBB, 1981; CADÉE, 1986; CADÉE and HEGEMAN, 1991, 1993; SMAYDA, 1990; HICKEL *et al.*, 1992). The annual primary production in the western Dutch Wadden Sea was recently found to be closely and statistically significantly correlated to the discharge of dissolved inorganic phosphate from the River Rhine via Lake IJssel (DE JONGE, 1990). Therefore, it was concluded that phosphate may still be limiting phytoplankton growth in the Wadden Sea (DE JONGE, 1990; DE JONGE and ESSINK, 1991). Phosphate limitation seems to be a common feature in Dutch and German coastal waters (PEETERS and PEPERZAK, 1990; BAUERFEIND *et al.*, 1990), probably terminating the spring bloom of *Phaeocystis pouchetii* (VELDHUIS *et al.*, 1986), although also nitrogen may become growth limiting for phytoplankton growth, especially in summer (RIEGMAN *et al.*, 1990).

In the coastal zone, the concentrations of dissolved inorganic phosphate are governed not only by runoff but also by physical, geochemical and biological processes in rivers and their estuaries. In the Ems estuary, these processes result in a non-conservative gradient of dissolved inorganic phosphate. In the mid-estuarine reaches a maximum in dissolved inorganic phosphate is present which attains highest values during summer (DE JONGE and VILLERIUS, 1989). Biological mineralization undoubtedly contributes to this pattern (VAN ES, 1982). The dissolved inorganic phosphate distribution in the Ems estuary, however, may also be the result of the transport and behaviour of calcite on one side, and of the ability of clay minerals to adsorb dissolved inorganic phosphate under the local estuarine conditions on the other (DE JONGE and VILLERIUS, 1989). DE JONGE and ENGELKES (1993) further showed that iron(oxy)hydroxides play a crucial role in the phosphorus cycle in the Ems estuary.

Because of the importance of iron in the phosphorus cycle (FOX, 1989; BOERS *et al.*, 1993) the seasonal behaviour of dissolved inorganic phosphate and iron in the Ems estuary were studied in relation to that of dissolved aluminium. Aluminium was included in this study because its geochemistry in coastal water is determined by adsorption/desorption processes.

ses with suspended matter and possibly also by iron geochemistry (VAN BEUSEKOM, 1988).

In this paper we focus on a restricted data set obtained during four sampling cruises in winter 1992/1993, because potentially interfering biological processes are at a minimum then.

## 3 Materials and methods

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### 3.1 Study area

The study was carried out in the estuary of the River Ems, situated on the border between The Netherlands and the Federal Republic of Germany (Fig. 1). As a rain fed river, the discharge of the River Ems varies strongly, averaging c.  $115 \text{ m}^3 \text{ s}^{-1}$ . The tidal limit is at the weir near Herbrum. The estuary is c. 100 km long. The tidal prism in the inlet between the barrier islands of Rottumeroog and Borkum is approx.  $10^9 \text{ m}^3$ . The mean tidal range increases from 2.3 m near the barrier islands to 3.2 m at Emden (DE JONGE, 1983).

A complicated geomorphology and strong tidal currents result in a complex pattern of water currents and a steep salinity gradient (DE JONGE, 1992). There is a mean suspended matter gradient from approx.  $20 \text{ mg dm}^{-3}$  near the tidal inlet to approx.  $400 \text{ mg dm}^{-3}$  in the most turbid part of the estuary (DE JONGE, 1988). In the Dollard (see Fig. 1), the mean suspended matter concentration is c.  $200 \text{ mg dm}^{-3}$ .

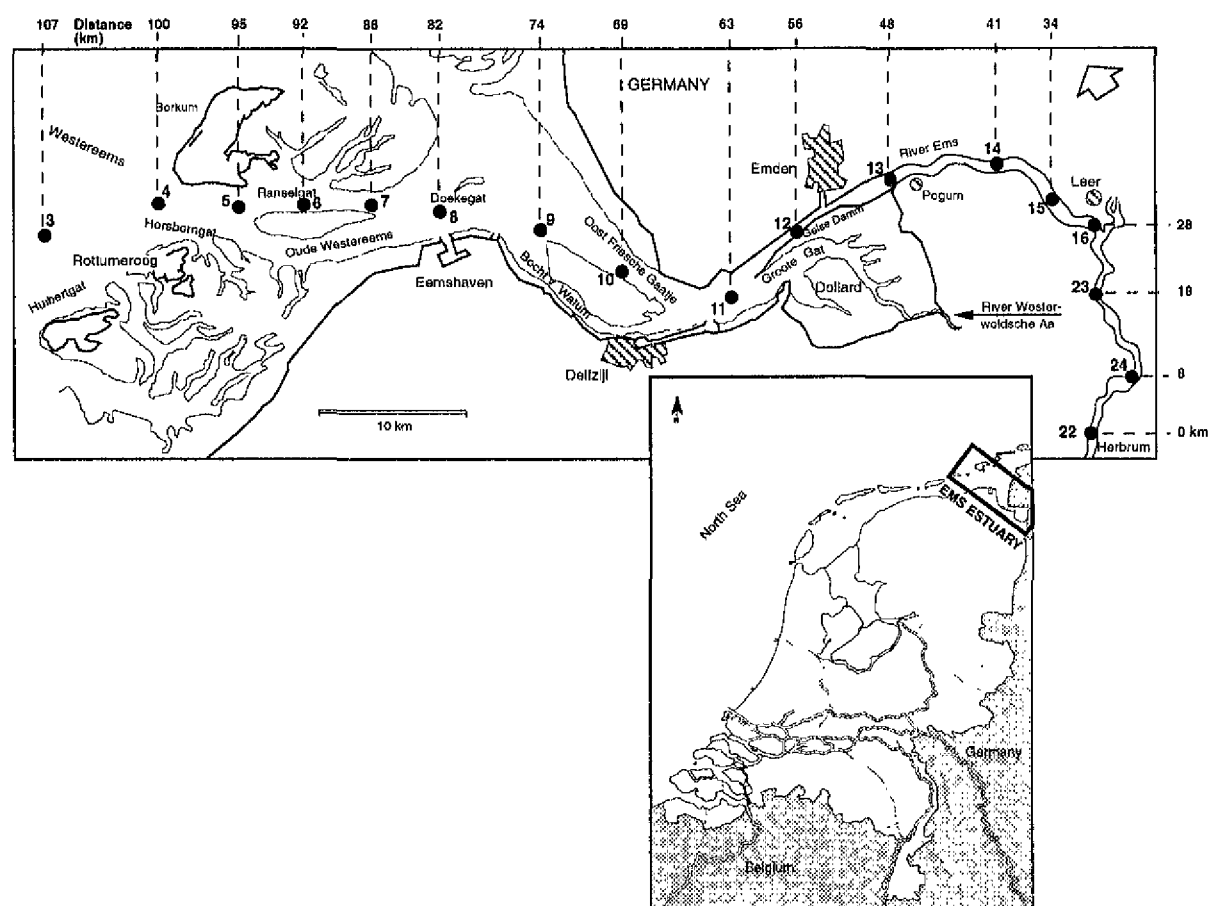
### 3.2 Sampling

Between mid-November 1992 and mid-February 1993, water samples were taken at approximately monthly intervals (24-25/11/1992, 9-10/12/1992, 12-13/01/1993 and 09-10/02/1993) at stations shown in Fig. 1. Samples were taken with a pumping device from 1.5 m below the surface. In addition, surface water samples from the River Ems upstream of the weir near Herbrum (St. 22) and between Herbrum and Leer (St. 23 and 24) were taken. All surveys started at the seaward station (1) just before high water. Because of adverse weather conditions stations 1-4 could not be sampled in January 1993.

Water samples for the analysis of dissolved nutrients were filtered on board using Whatman GF/C filters. The filtrate was frozen immediately and stored at  $-20^\circ\text{C}$  until analysis. Water samples for dissolved aluminium and iron were filtered through  $0.45 \mu\text{m}$  nucleopore polycarbonate membrane filters mounted in polycarbonate filtration units. The samples for dissolved aluminium were directly transferred into teflon reaction bottles and stored dark and cool ( $+4^\circ\text{C}$ ) until analysis.

**Figure 1**

Map of the Ems estuary with sampling stations and distances (km) from the weir at Herbrum. Stations 1 and 2 are situated at 15 km and 8 km west of station 3.



The filtrate for dissolved iron was acidified by adding 100  $\mu$ l suprapure  $\text{HNO}_3$  (65%) to 100 ml of sample. These samples were stored at +4°C until analysis. All sample handling was carried out in a clean bench.

To avoid contamination, the nucleopore filters were rinsed by passing 250 ml of nanopure water. All other plastic ware used was first cleaned with a hot detergent, rinsed with hot tap water and nanopure water, acid-cleaned with 1N  $\text{HNO}_3$  and again rinsed thoroughly with nanopure water. The polyethylene bottles to store the water samples meant for iron measurements were first cleaned with hot detergent, rinsed with hot tap water and nanopure water, soaked for 20 minutes in 0.07% ascorbic acid, soaked overnight in 1.5N  $\text{HNO}_3$ , rinsed again thoroughly with nanopure water.



and filled with  $\sim 0.0001\text{N HNO}_3$  which was discarded shortly before being used.

### 3.3 Analyses

Conductivity was measured with a WTW conductometer and converted to practical salinity units (PSU). pH was measured potentiometrically with a WTW pH meter. Suspended matter was determined gravimetrically on glasfiber filters (GF/C, Whatman) after screening through a  $55\text{ }\mu\text{m}$  mesh sieve to remove sand and coarse organic matter. The deepfrozen samples for nutrient analysis were quickly thawed at  $75^\circ\text{C}$  and analyzed on a Technicon autoanalyzer. Phosphorus compounds were determined according to the Dutch modification of Industrial Method 113-73W (based on MURPHY and RILEY, 1962). Concentrations of nitrogen were determined according to GRASSHOFF *et al.* (1983). Dissolved iron was measured after STOOKEY (1970) using ascorbic acid as a reductant. Dissolved aluminium was analyzed immediately using the Lumogallion method after HYDES and LISS (1976). This method is based upon the formation and measurement of the fluorescent Al-Lumogallion complex at pH 5. These measurements, however, had to be corrected for a strong signal of natural fluorescence due the high DOC content of the river Ems. Furthermore, the high iron content of the River Ems interferes with the Lumogallion method. Therefore, each measurement in samples of low salinity and in freshwater samples, was calibrated by standard addition ( $250\text{ nmol dm}^{-3}\text{ Fe}$ ) to a subsample. The natural fluorescence measured during the aluminium analysis was used as an indication of dissolved organic carbon (DOC, see CADÉE and LAANE, 1983). The emission and excitation wavelengths (470 and 590, resp.) were the same as used for the aluminium determination.

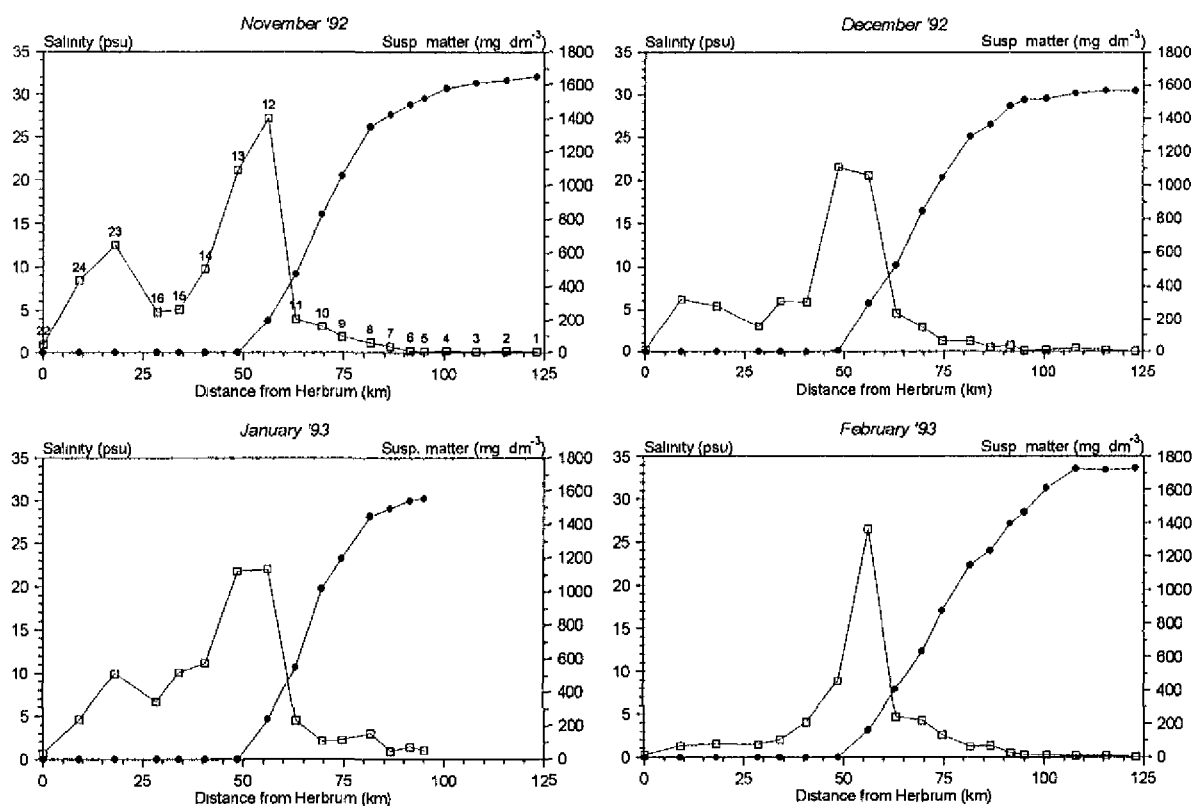


## 4 Results

The longitudinal salinity distributions (Fig. 2) show a steep gradient over a distance of 40 km between the Island of Borkum (km 90) and Emden (km 50). Upstream of Emden no contribution of sea water was detectable. Suspended matter (Fig. 2) shows two concentration peaks.

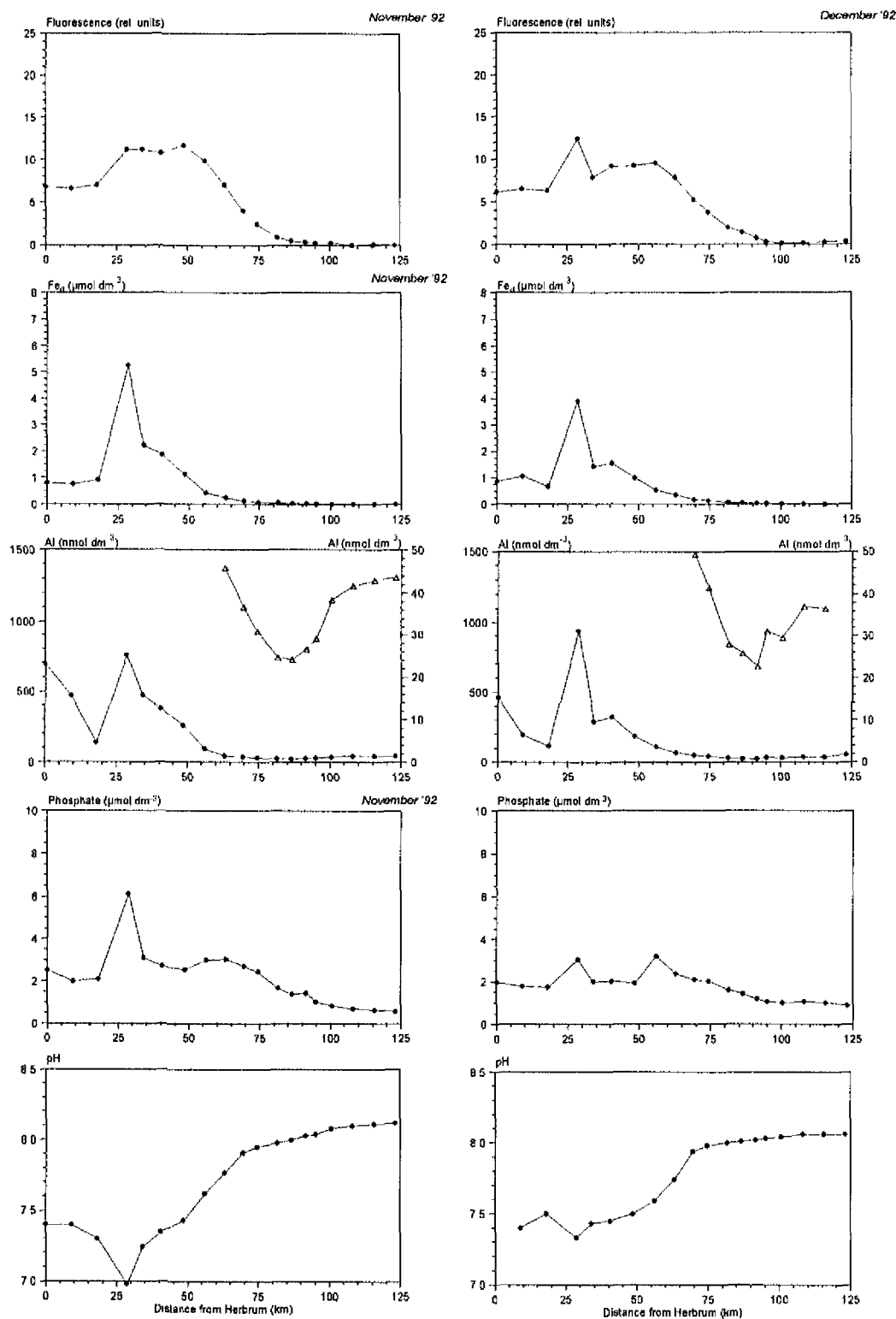
Figure 2

Longitudinal distribution of salinity (closed symbols) and suspended matter (open symbols) in the Ems estuary on 4 sampling occasions. Station numbers are indicated in the upper left panel.



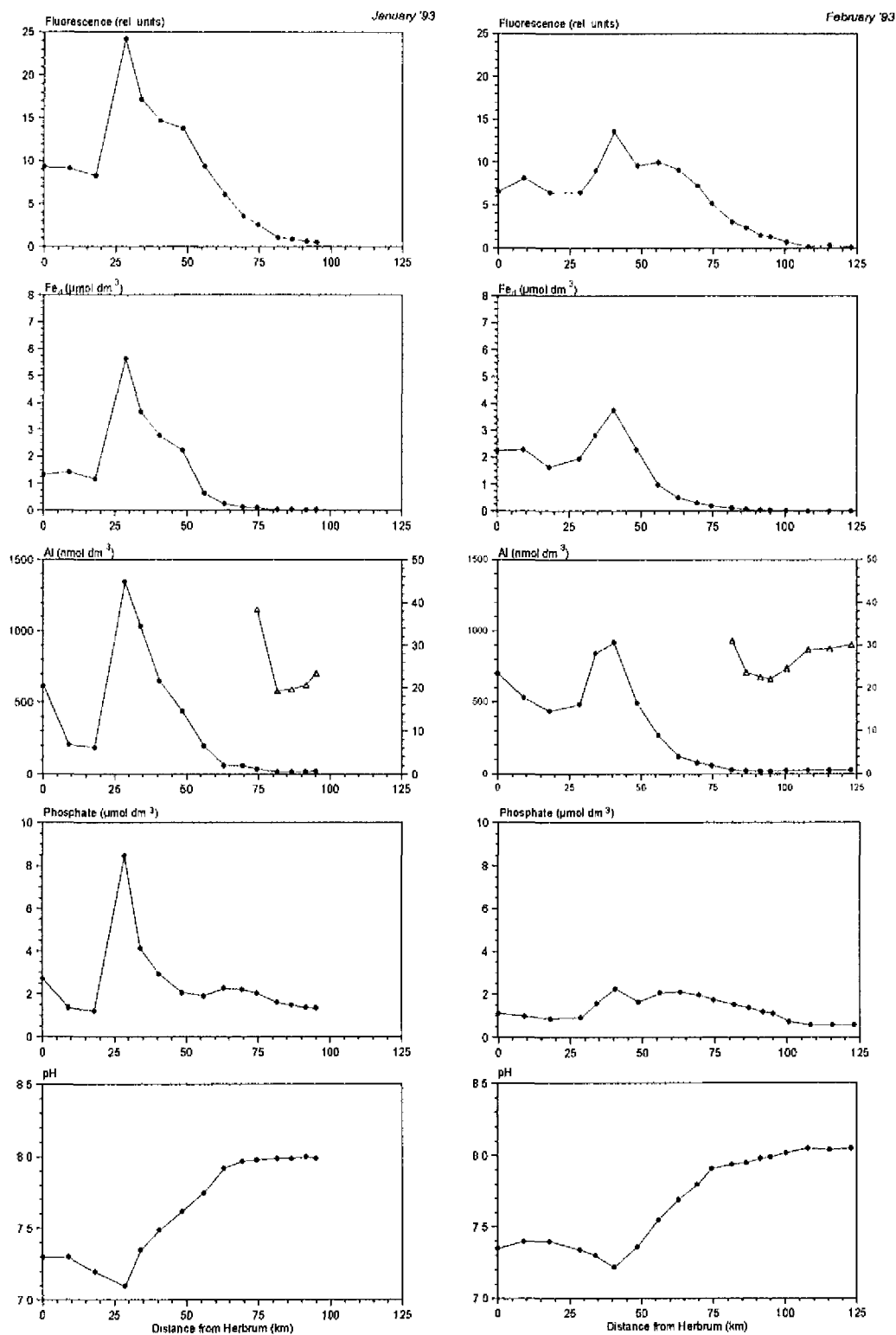
**Figure 3**

Longitudinal distribution of fluorescence, dissolved iron, dissolved aluminium, dissolved inorganic phosphate and pH in the Ems estuary during winter. Aluminium concentrations in the outer part of the estuary are also shown scaled up (triangles) to reveal the minimum around km 80-95.



**Figure 3**

Longitudinal distribution of fluorescence, dissolved iron, dissolved aluminium, dissolved inorganic phosphate and pH in the Ems estuary during winter. Aluminium concentrations in the outer part of the estuary are also shown scaled up (triangles) to reveal the minimum around km 80-95.



One, at the transition zone between brackish and freshwater (km 50), with suspended matter concentrations up to  $1200 - 1400 \text{ mg dm}^{-3}$ . Downstream the turbidity maximum (between km 40 and 60) the suspended matter concentrations decreased to values of  $20 \text{ mg dm}^{-3}$  within a distance of 40 km. Also in upstream direction there is a strong decrease in the suspended matter concentrations. Just upstream of the weir at Herbrum (km 0) the values are as low as near the sea.

Distribution patterns of fluorescence, dissolved iron, aluminium and dissolved inorganic phosphate and pH are presented in Figure 3. The fluorescence shows values of 6 - 9 relative units in the freshwater part at the very head of the estuary (km 0 - 25). Further downstream, but still in the freshwater zone a clear peak in fluorescence is observed. Downstream of km 50 fluorescence gradually decreases.

The distribution of dissolved iron in the freshwater part of the estuary resembles that of fluorescence. Between km 0 and 25 concentrations range from  $0.8$  to  $2.2 \text{ } \mu\text{mol dm}^{-3}$ . A little downstream of km 25 a sharp maximum is observed during all four cruises with concentrations of  $3.7$  to  $5.3 \text{ } \mu\text{mol dm}^{-3}$  followed by a gradual decrease to values below  $0.05 \text{ } \mu\text{mol dm}^{-3}$  at sea.

The aluminium distribution differs only slightly from the pattern described above. The concentrations upstream of the weir ( $461 - 702 \text{ nmol dm}^{-3}$ ) rapidly decrease downstream to values of  $115 - 439 \text{ nmol dm}^{-3}$  followed by a maximum at km 28 ( $757 - 1346 \text{ nmol dm}^{-3}$ ) which coincides with peaks in both fluorescence and dissolved iron. Seaward of this maximum, the dissolved aluminium concentrations rapidly decrease and reach minimum values of  $19$  to  $23 \text{ nmol dm}^{-3}$  between km 80 and 95. Further seaward, dissolved concentrations increase again to reach c.  $44 \text{ nmol dm}^{-3}$  in November 1992. These sea water concentrations gradually decreased to  $30 \text{ nmol dm}^{-3}$  in February 1993.

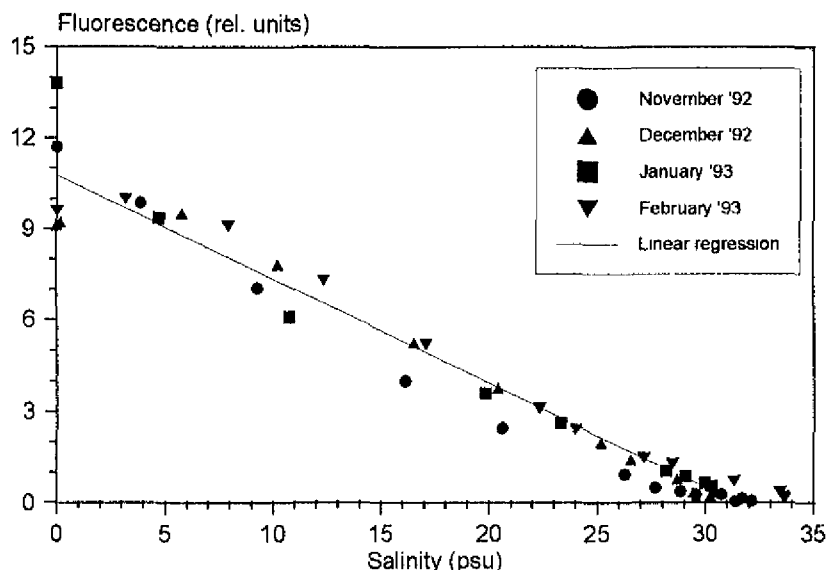
Dissolved inorganic phosphate concentrations in the river ranged from  $1.1$  to  $2.7 \text{ } \mu\text{mol dm}^{-3}$ . They first decrease slightly in the freshwater part between km 0 and 25 followed by a maximum of  $2.3$  to  $8.5 \text{ } \mu\text{mol dm}^{-3}$  at km 28. Downstream of this maximum the concentrations first tend to decrease until a secondary maximum ( $2.3 - 3.0 \text{ } \mu\text{mol dm}^{-3}$ ) can be noticed in the mid-estuary near km 60. From here the phosphate concentrations decrease again to  $0.6 - 0.9 \text{ } \mu\text{mol dm}^{-3}$ .

The pH in the River Ems varies between  $7.3 - 7.4$ , dropping to  $7.0 - 7.3$  in the freshwater part of the estuary (km 28 - 40). Downstream of this minimum pH values gradually increase to c.  $8.0$  near km 80. In the seaward part of the estuary the pH is around  $8.1$ .

Despite the similar distribution patterns of fluorescence and dissolved iron, aluminium and dissolved inorganic phosphate in the fresh water part of the estuary, these compounds behaved differently during estuarine mixing.

**Figure 4**

Linear regression of fluorescence data plotted against salinity over the entire salinity gradient ( $P < 0.001$ ;  $r = 0.98$ ). Because of the local maximum in the freshwater zone (cf. Fig. 3), the data collected within the freshwater zone are not presented.

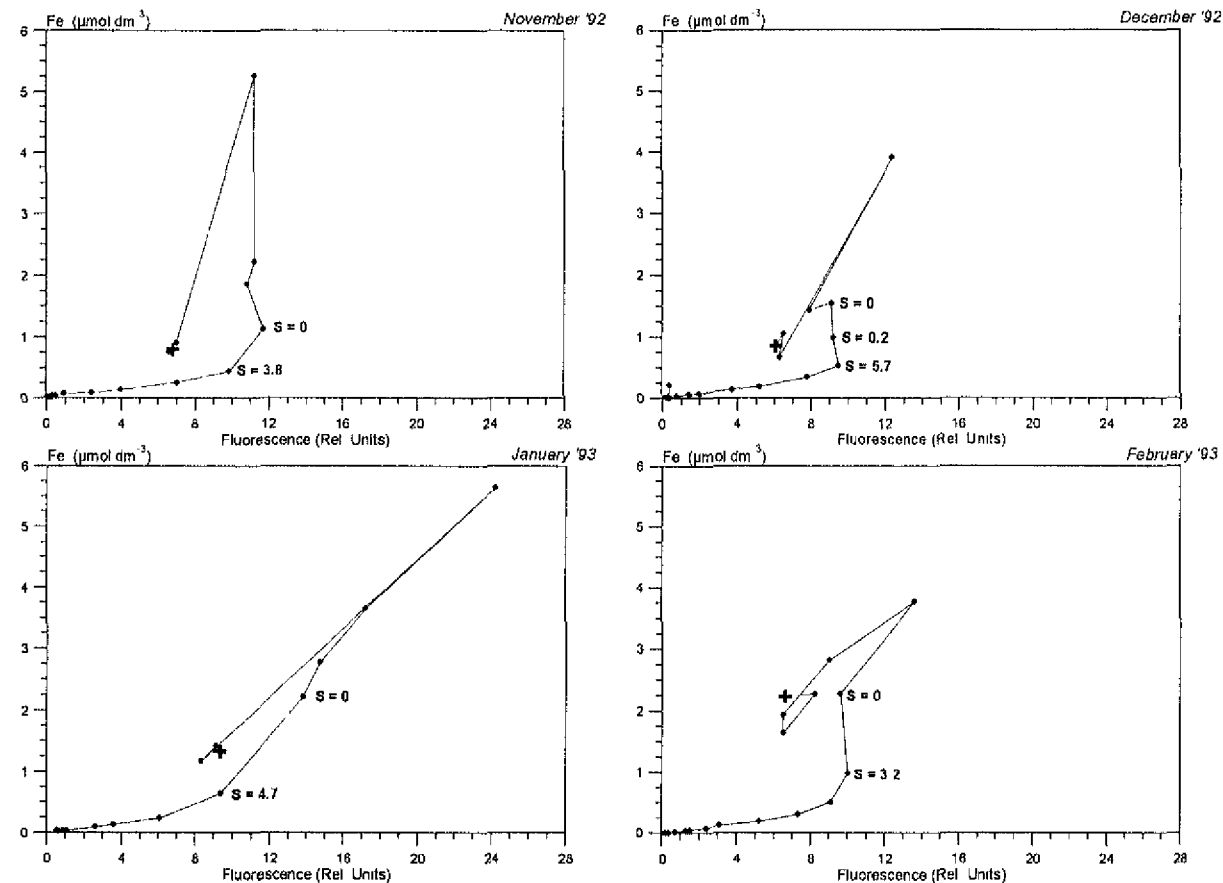


In Figure 4 all data on fluorescence including the last sample from the freshwater part of the estuary (thus, data from km 0 to 40 excluded) are plotted against salinity. The high correlation coefficient ( $r = 0.98$ ;  $P < 0.001$ ) substantiates the conservative behaviour of fluorescence during estuarine mixing. It further indicates that the large variation in fluorescence observed upstream of the turbidity maximum is stabilized before estuarine mixing starts. The fluorescence at zero salinity estimated from the linear regression amounts to 10.8 relative units whereas the mean river fluorescence (at km 0) amounts to 7.2 relative units indicating an extra fluorescent matter input of c. 3 relative units within the freshwater part of the estuary (Fig. 2).

Figure 5 shows plots of dissolved iron versus fluorescence for the four cruises. Within the freshwater zone a high correlation exists during the augmentation and removal of both dissolved iron and fluorescence. At the first station with a salinity  $> 0$  this correlation disappears and dissolved iron concentrations quickly drop to  $0.3 \mu\text{mol dm}^{-3}$  at a fluorescence of 8 relative units which equals a salinity of approximately 7 PSU. At higher salinities, dissolved iron again correlates well with fluorescence ( $r = 0.98$ ) showing similar slopes for all winter samplings (Fig. 6). The longitudinal distributions of dissolved iron and aluminium show similar patterns, except for the fast drop of the high riverine aluminium concentrations in the upper part of the estuary (see Fig. 3).

**Figure 5**

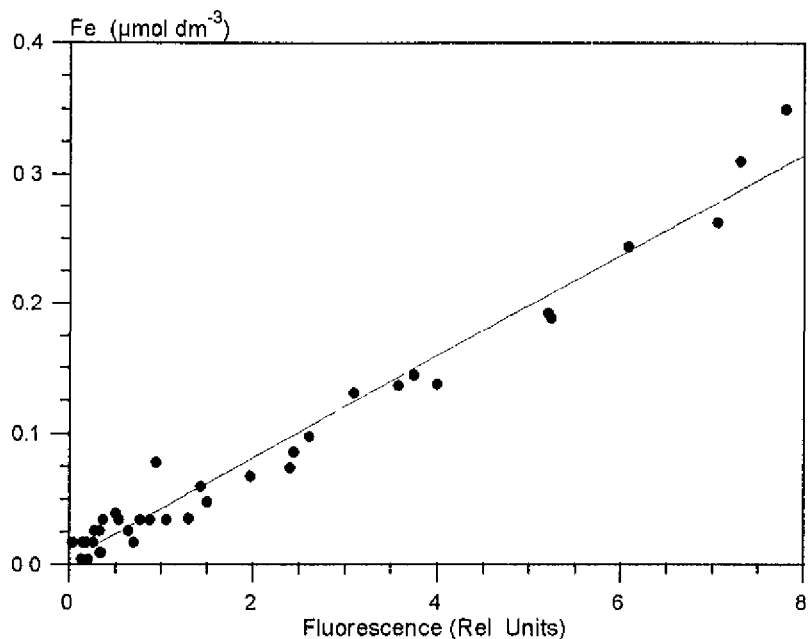
Changing relationship between dissolved iron and fluorescence during winter samplings when going from river to sea. The river sample upstream of the weir is indicated by symbol +. Some observed salinities (S) are indicated.





**Figure 6**

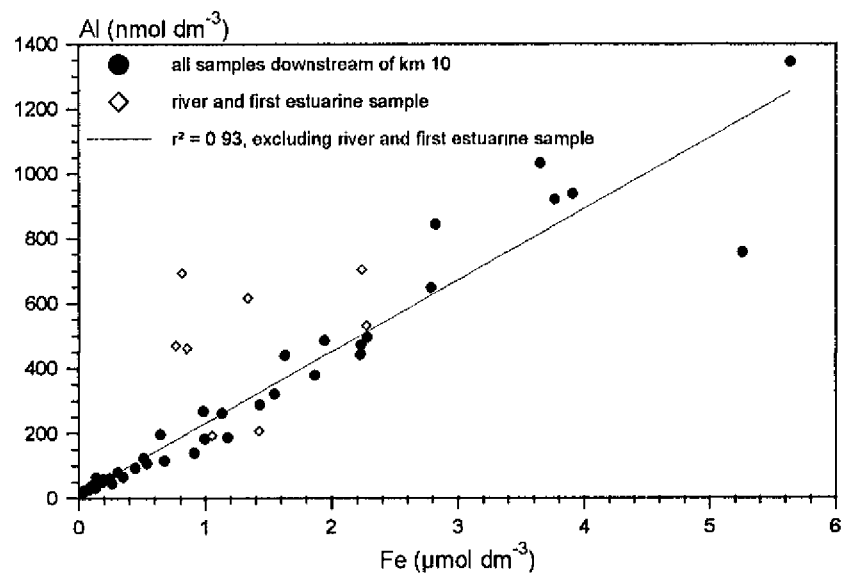
Linear regression of dissolved iron on fluorescence for all stations on all cruises with brackish water (salinity > 0) and a fluorescence < c. 8 relative units ( $P < 0.001$ ;  $r = 0.96$ ).



In Figure 7 all aluminium data were plotted against dissolved iron. In general both elements correlate very well. When excluding the river stations at km 0 and 8, a correlation coefficient of 0.96 emerges, indicating that also in most of the fresh water and in the entire brackish part of the estuary the augmentation and subsequent removal of both metals (*cf.* Fig. 3) are tightly coupled.

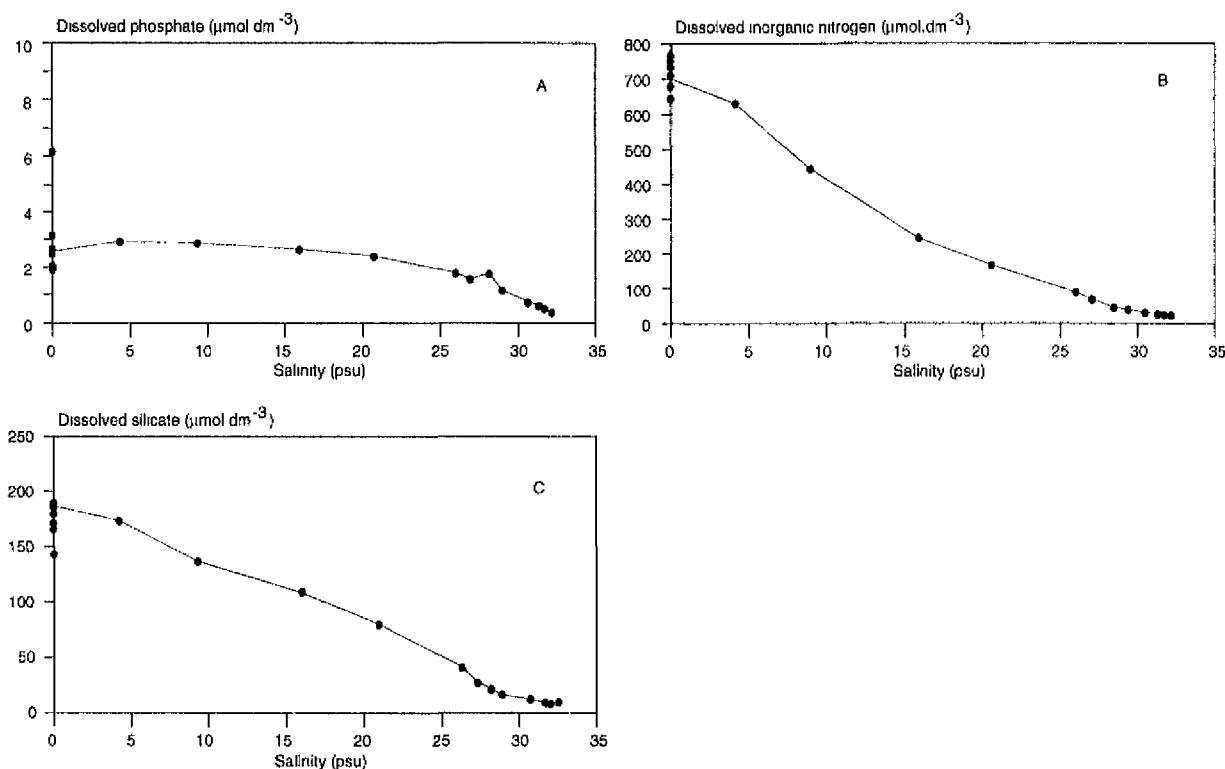
**Figure 7**

Plot of all dissolved aluminium data against dissolved iron. Linear regression based on all values downstream of km 10 (filled circles;  $P < 0.001$ ;  $r = 0.96$ ). Observations indicated by diamond are from stations at 0 and 8 km (*cf.* Fig. 1).



**Figure 8**

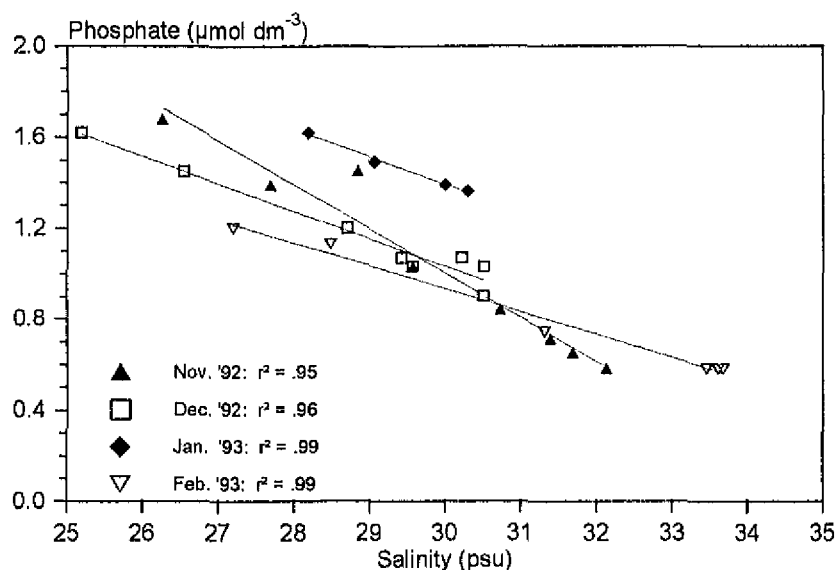
Examples of plots of dissolved inorganic phosphate (DIP), dissolved inorganic nitrogen (DIN) and silicate against salinity



In Figure 8A dissolved inorganic phosphate is plotted against salinity. A non-conservative mixing characterized by mid estuarine "production" is present during all four cruises. The location of the mid-estuarine maximum in dissolved inorganic phosphate ( $2.3 - 3.0 \mu\text{mol dm}^{-3}$ ) varies and is found at salinities between 5 and 15. At salinities above 25 dissolved inorganic phosphate mixes conservatively with sea water (Fig. 9). The estimate of dissolved inorganic phosphate at zero salinity by extrapolation of the linear regression varied not much ( $6.8 \mu\text{mol dm}^{-3}$  in November,  $4.7 \mu\text{mol dm}^{-3}$  in December,  $5.1 \mu\text{mol dm}^{-3}$  in January and  $4.0 \mu\text{mol dm}^{-3}$  in February). This may indicate that the Ems estuary does not act as a filter for dissolved inorganic phosphate.

**Figure 9**

Relationship between dissolved inorganic phosphate and salinity at salinities > 25 PSU. For each cruise the linear regression is drawn (November  $P < 0.001$ ;  $r = 0.97$ , December  $P < 0.001$ ;  $r = 0.98$ , January  $P = 0.004$ ;  $r = 0.99$ , February  $P < 0.001$ ;  $r = 0.99$ ).



Only in December the distribution of DIN (Fig. 8B) shows an entirely conservative distribution pattern. In November the concave curve indicates that shortly before sampling the DIN load to the Ems estuary was increased. The convex curve in January and February indicate decreasing DIN loads from the river Ems.

The plots of silicate (Fig. 8C) in the reaches between Eemshaven and Borkum show for cruises 10, 11 and 13 a linear relationship with salinity. The silicate concentrations in the fresh water are approximately 200 µM. The distribution during the sampling of cruise 12 deviates from the other three. The very low concentrations in the middle reaches of the estuary suggest that during the analysis procedure something went wrong; therefore these data are not further used for discussion.

Table 1 gives information relevant to the possible filter function of the Ems estuary. From the results it is clear that the Ems estuary mainly functions as a transit area for DIN. Only 15% is filtered in the estuary.

All the silicate is transported to the sea. Moreover, compared with the river load, another 7% of silicate is released to the water column within the estuary.

The distribution of DIP shows a different picture. During all surveys a maximum was discernible in the middle reaches of the estuary, indicating desorption of DIP from suspended matter and/or release from bottom sediments. This possibly is connected to the geochemical behaviour of DIP in relation to iron. The by extrapolation calculated river concentrations (weighed means) are 1.9 to 3.6 times higher than the measured values.

**Table 1**

Comparison of nutrient concentrations in the river Ems and Westerwoldsche Aa (weighted mean) with estimates based on linear regression analysis between salinity and nutrient concentrations. For DIN and silicate the data with salinities greater than 10 PSU have been used. For DIP the data with salinities greater than 25 PSU have been used.

	Weighted mean Ems and WWA  ( $\mu\text{M}$ )	Extrapolation zero salinity  ( $\mu\text{M}$ )	Regression coefficient (r) and significance level (P)	Input/Retention  (%)
DIN	667	570 $\pm$ 24	$r^2 = 0.96$ ; $P < 0.0001$	- 15
cruise 10-13				
Silicate	199	208 $\pm$ 6.7	$r^2 = 0.98$ ; $P < 0.0001$	+ 7
cruise 10, 11, 13				
DIP				
cruise 10	2.48	6.8 $\pm$ 1.4	$r^2 = 0.95$ ; $P < 0.0001$	+274
cruise 11	1.98	4.7 $\pm$ 0.7	$r^2 = 0.96$ ; $P < 0.0001$	+237
cruise 12	2.65	5.1 $\pm$ 1.0	$r^2 = 0.99$ ; $P < 0.005$	+192
cruise 13	1.12	4.0 $\pm$ 0.5	$r^2 = 0.99$ ; $P < 0.0001$	+357
all cruises	2.06	5.2		+252

## 5 Discussion

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### 5.1 Longitudinal distribution pattern

**Longitudinal distribution pattern** The longitudinal distributions of fluorescence, dissolved iron, aluminium and dissolved inorganic phosphate and of pH show two distinct estuarine regions viz. the freshwater zone (between the weir at Herbrum and Emden) and the salinity gradient (between Emden and Borkum). In the freshwater zone, a local maximum of the above mentioned parameters including a maximum in  $H^+$  concentration was observed. In the salinity gradient, only fluorescence showed conservative behaviour. Of the other parameters, dissolved aluminium and iron quickly disappeared from the dissolved phase and reached minimum values coinciding with the mid-estuarine maximum in dissolved inorganic phosphate. The extension of the zone of aluminium and iron removal and of secondary phosphate increase shows a marked overlap with the zone where pH values increase from 7.2 - 7.4 in the freshwater part of the estuary to 8.1 in sea water. In the outer estuary fluorescence, dissolved iron and dissolved inorganic phosphate mix conservatively with sea water indicating that the estuary acts as a source of these substances for the North Sea, whereas it clearly acts as a sink for dissolved aluminium from marine origin. Interesting is that both the augmentation and a large part of the removal of aluminium, iron, phosphorus and DOC occur within the freshwater zone of the estuary.

To facilitate discussion, the observed gradients are summarized schematically in Figure 10. The local maxima in the freshwater zone can either be advective or due to local processes. Theoretically, short-term variations in the discharges of Ems water can cause a downstream maximum in solutes. Our measurements, however, indicate that in the river values were always lower than in the estuary. Moreover, it is unlikely that variations in fluorescence and other compounds in the River Ems were missed by our sampling programme. Still with the exception of February 1993 a peak occurred near Leer at km 28. Also CADÉE and LAANE (1983) noticed a maximum in fluorescence during two winter cruises in 1982 at km 28. An other possible explanation for the observed local maxima is input of high loads of fluorescence from the River Leda discharging into the River Ems. Unfortunately, no measurements are available yet for the Leda. CADÉE and LAANE (1983), however, made it acceptable that the River Leda is not responsible for the observed maxima. Since, the ratio between fluorescence and DOC in the riverine samples and in the local fluorescence maxi-

mum were not different, these authors interpreted that the extra DOC in the maximum had originated from the River Ems itself and not from an external source. An external source would most probably have had a different fluorescence-DOC ratio. The constant aluminium-iron ratio both upstream, within and downstream of the maximum (Fig. 7) also favours local rather than advective factors as being responsible for the observed maximum.

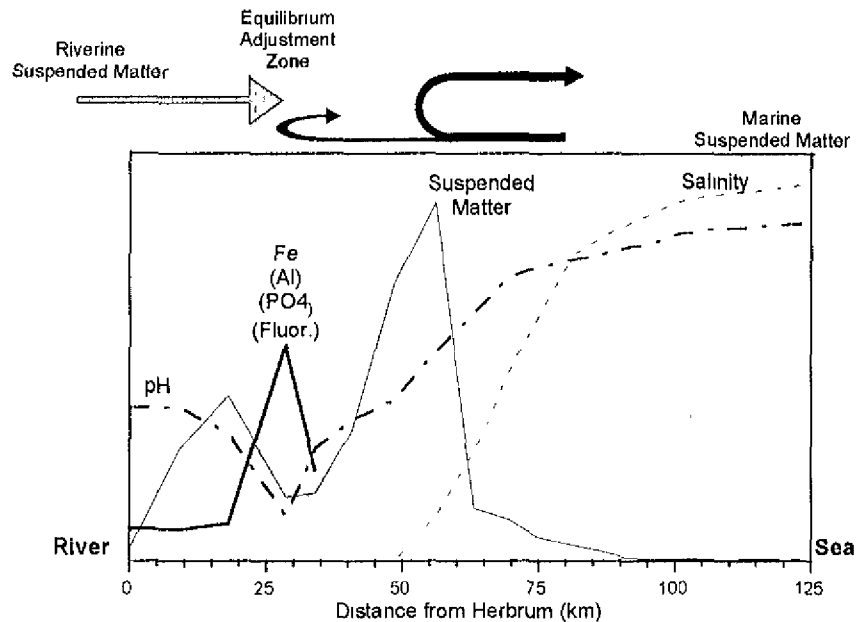
Although the maxima in the freshwater part of the estuary were mostly found at km 28, their position was shifted approximately 20 km downstream during February 1993 after a period of high run-off. This phenomenon is considered an extra argument against the river Leda being an external source of fluorescence and dissolved iron, aluminium and dissolved inorganic phosphate.

CADÉE and LAANE (1983) presented several explanations for the increase in DOC and fluorescence in the freshwater part of the estuary. They noticed that the distinction between DOC and POC is of arbitrary nature, organic carbon is present in a continuous size spectrum (e.g. MACKINNON, 1981). Thus, the increase in "dissolved fluorescence" might simply be caused by increased amounts of very fine particles not retained by filters. They also suggested that the increase in DOC (fluorescence) might be the result of a shift between the POC-DOC equilibrium due to physical and chemical changes of suspended matter in the turbidity maximum. We support the view of CADÉE and LAANE (1983) that a shift in the DOC-POC equilibrium is the most probable explanation for the in situ production of DOC. However, in our opinion the reason for this shift is not a change in particulate matter characteristics during its presence in the turbidity maximum. On the contrary, our results show that the observed maxima are always upstream of the turbidity maximum. Therefore, the high iron-fluorescence ratios upstream and within the maximum compared to low ratios downstream of the turbidity maximum suggest a riverine rather than a marine source.

Since the maxima are characteristic for the freshwater tidal part of the estuary and not for the pure riverine part of the Ems (Fig. 10) the observed distribution of DOC, dissolved iron, aluminium and dissolved inorganic phosphate may be explained by the mechanism described by POSTMA and KALLE (1955) and POSTMA (1981), viz. estuarine circulation concentrating suspended matter in the low salinity region. However, temporarily (slack-neap tide) also sedimentation takes place of this material (WELLERSHAUS, 1981) resulting in shoals that are eroded during sufficiently turbulent conditions at half tide and spring tide. The interaction between the tidally moving freshwater - saline water interface and the settlement of suspended sediment from the turbidity maximum can easily explain the upstream transport of marine suspended matter beyond the turbidity maximum to well within the freshwater tidal zone of the Ems estuary.

**Figure 10**

A summary diagram representing the longitudinal distributions of salinity, suspended matter, pH and dissolved iron in the Ems estuary during winter. The iron curve also represents the relative distributions of dissolved aluminium, dissolved inorganic phosphate and fluorescence. This curve is drawn only in the freshwater part of the estuary because these 4 compounds show a different longitudinal concentration distribution in the salinity gradient (cf. Fig. 3).



EISMA *et al.* (1985) examined the nature of suspended matter in the Ems estuary and showed that the particles within the turbidity maximum were of marine origin. The mixing of marine particles with riverine particles occurred mainly in the freshwater tidal zone of the Ems estuary, the steepest gradients being observed upstream of Leer (km 28). Further evidence for the intrusion of marine particles into the freshwater zone has been presented by SALOMONS (1973).

Interestingly, the transition zone between marine and riverine suspended matter coincides with the freshwater maxima discussed above. We therefore suggest that the local increase of dissolved aluminium, iron, DOC and  $H^+$  is caused by the interaction of freshwater and its solids with suspended matter of marine origin (Fig. 10). We envisage this interaction as follows: On marine particles ligand exchange sites are in equilibrium with respect to the ions in sea water. When such particles are transported into the freshwater zone, with a quite different ionic composition, a new equilibrium has to be established between the solid and dissolved phase. In a mixture of riverine and marine sediment particles (such as present in the freshwater zone near Station 16) adsorbed marine ions get redistributed from the marine to the riverine solids. Thus, at the river-sea interface a change in the POC-DOC equilibrium can be induced resulting in the release of DOC and DOC-associated iron and aluminium. BOYLE *et al.* (1977) discussed the iron-DOC relationships in estuarine waters and presented evidence that DOC can keep iron(oxy)hydroxide particles in solution through the formation of colloids. DOC-iron complex formation was thought to be less important. Addition of especially magnesium and calcium can cause the break-up of the DOC-iron association after which iron precipitates and

DOC remains in solution. Whether the aluminium-DOC and iron-DOC relationships in the Ems estuary are based upon colloids or ligand formation is difficult to assess on the basis of the present results. However, there seem to be at least two types of iron-DOC relationships. Possibly, one type is easily broken up within the brackish- and freshwater part of the estuary under influence of present marine particles. The other type possibly consists of a stable iron-DOC complex that is not broken up. We suggest that these two types represent either DOC-stabilized iron colloids or stable iron-DOC complexes. Further knowledge on the nature of the above mentioned processes is important since the high reactivity of young iron

(oxy)hydroxides (formed during ligand exchange processes) compared to aged hydroxides (liberated during the break up of the DOC-iron colloids) is well known (e.g. SINGH and SUBRAMANIAN, 1984). Such knowledge is ecologically important since the dynamics of dissolved inorganic phosphate in the marine and estuarine environment are strongly influenced by iron hydroxides (FOX, 1989; DE JONGE and ENGELKES, 1993; DE JONGE *et al.*, 1993; BOERS *et al.*, 1993). The above mentioned factors and processes will influence the availability and exchangeability of the phosphate that is remobilized within the freshwater part of the estuary both by chemical processes and by the remineralization of fresh organic matter

#### 5.1.1 Iron - phosphorus relationship

The concentrations of dissolved inorganic iron and dissolved inorganic phosphate are to a large extent determined by their reactivity with iron-(oxy)hydroxides (FOX, 1988, 1989). However, the formation and dissolution of authigenic clay minerals have been suggested to explain the low salinity removal and mid-estuarine input of dissolved aluminium (MACKIN and ALLER, 1989), although also adsorption onto suspended matter (MORRIS *et al.*, 1986) or onto iron(oxy)hydroxides (VAN BEUSEKOM, 1988) may explain the dynamics of dissolved aluminium in estuarine areas. Equilibria between dissolved and, mainly iron(oxy)hydroxide associated, particulate phosphate (FOX, 1993; DE JONGE and ENGELKES, 1993) buffer the dissolved inorganic phosphate concentrations over a large part of the estuary. In contrast, the distribution patterns of dissolved iron show no buffering but a rapid removal instead. The large variations in dissolved iron are apparently related to its presence as DOC colloids and complexes and to their behaviour within the estuary. Because of the low solubility of iron (FOX, 1988) true inorganic iron species only play a minor role.

#### 5.1.2 Iron - aluminium relationship

The relationship between aluminium and iron (Fig. 7) suggests that within the fresh water and low salinity range the dynamics of dissolved aluminium were related to the release and destruction of aluminium-DOC colloids or complexes and to the adsorption of inorganic dissolved aluminium onto suspended matter. In the low salinity range the distribution patterns of aluminium and iron differs. While the DOC-stabilized iron has a similar concentration both upstream and downstream the weir of Herbrum (km 0), dissolved aluminium is quickly removed from solution downstream the



weir. That aluminium is not removed upstream of the weir is possibly caused by the low concentrations of suspended matter in the river. These results are comparable to those of MORRIS *et al.* (1988) for the Tamar estuary. That dissolved aluminium and not dissolved iron is removed directly downstream of the weir, is possibly due to the fact that dissolved aluminium is present as both inorganic and organic species of which only the inorganic species is removed. This assumption is supported by Figure 7 where it is shown that for most of the estuary both compounds correlate very well whereas the outliers from the river (km 0) and the first estuarine station (km 8) mostly have higher aluminium concentrations than predicted by the regression line. This indicates the presence of an other, particle reactive, inorganic species that is not stabilized and sensitive to the presence of high concentrations of suspended matter.

### 5.1.3 Clay minerals - aluminium relationship

The formation and dissolution of authigenic clay minerals, suggested by MACKIN and ALLER (1989) to explain the removal and augmentation of dissolved aluminium in estuaries probably plays a minor role in the Ems estuary. It is interesting to note that the dissolved aluminium concentrations in the North Sea are higher than in the estuary proper. Whether this is due to a higher affinity of aluminium to estuarine material than to seaborne material or to differences in concentrations remains to be answered.



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